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"GLOBAL TROPOSPHERIC EXPERIMENT AT THE HONG KONG ATMOSPHERIC CHEMISTRY MEASUREMENT STATION"

Final Report
(funding period: 1/1/95-12/31/95)

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KONG ATMOSPHERE CHEMISTRY
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Progress Report for NASA Grant NAG-1-1465
for the period 1 January - 31 December 1995
(including a 6-month no cost extension from 7/1/ - 12/31/95)

Principal Investigator: Mary Anne Carroll, University of Michigan
Postdoctoral Fellow: Dr. Tao Wang, University of Michigan

MAJOR ACTIVITIES:

- After discussing with the scientists at the HKPU, it was decided that research efforts before July 1995 would focus on data analysis and preparation of manuscripts, while maintaining the measurement station. Measurements/sampling included: O₃, CO, SO₂, NO, TSP (daily), RSP (daily), and ozone column density (continues, with a Brewer spectrophotometer). Significant progress was made in terms of station facilities with the installation of a second container that will be used to house additional instruments, store spare parts and serve as a on-site workplace.
- Data reduction of gas species data for the period during PEM-WEST (B) (February 17 to March 13, 1994) was completed. These data include: O₃, CO, NO, SO₂ and NO_y. Two versions were created (1 min and hourly-averaged).
- A data archive that contains surface meteorological data from the Hong Kong Royal Observatory and aerosol data from the University of Miami was created. Meteorological data include: temperature, dew point, wind speed and direction, mixing height, global radiation, and hours of sunlight. Aerosol data contains results of composition analysis and hourly averaged concentration of back carbon and scattering coefficient.
- A decision was made to include only data having a resolution better than one hour in a primary database to be used for data analysis. These hourly data include: O₃, CO, NO, SO₂, NO_y, black carbon, scattering coefficient, temperature, dew point, and wind speed and direction.
- Exploratory data analysis was performed, including examination of time series, frequency distributions, diurnal variations and correlation. Additionally, an expanded version of calculated backward air trajectories was obtained from Dr. John Merrill and used to compare with the surface observations. These exploratory analyses proved to be very valuable in identifying topics upon which manuscript preparation were based.

MAJOR RESULTS:

- Major scientific findings have been summarized in three separate manuscripts, two of which will be submitted to the 2nd NASA PEM-WEST B Data Workshop for the 1st round of review and discussions. The third one has

been submitted to the journal of Atmospheric Environment (see attached abstracts).

- Two extended abstracts based on the two manuscripts were submitted to the WMO/IGAC conference on Measurements and Assessment of Atmospheric Composition Change, to be held in Beijing, China, from October 19-23. The extended abstract for Dr. Wang's presentation is attached.
- Presentation by Dr. Wang at the HKPU/NASA PEM-West Workshop, October 18-20, 1995; abstract is attached.

Submitted to: The Journal of Geophysical Research
PEM-WEST B Special Issue

**Trace Gas Measurements During the Periods of Outflow from the
Asia Continent: Results from a Hong Kong Site During the PEM-
WEST (B)**

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ABSTRACT

Ozone, CO, NO, NO_y and SO₂ were measured at a relatively remote site in Hong Kong (22° 13'N, 114° 23'E, 60 m MSL) during the PEM-WEST B Experiment (February-March 1994). Concentrations of these species were strongly influenced by the continental outflow from Asia and particularly by the passages of cold fronts which periodically brought high levels of pollutants from the North. Averaged concentrations are 31±14 ppbv for O₃, 458±130 ppbv for CO, 9.33±7.84 ppbv for NO_y, and 1.31±1.46 ppbv for SO₂. CO appeared to be a good chemical indicator of changes of air mass types and its variability may be attributed to the relative strength of the outflow and to the transport of urban plumes. Variations of NO_y, SO₂ and black carbon appeared to be dominated by processes that occurred on relatively short time scales. Ozone was negatively correlated with CO and NO_y, suggesting that O₃ is chemically titrated by anthropogenic pollutants during the early stage of continental outflow. Winter-time mixing ratios of CO and ozone are significantly higher than those obtained in the summer (June) 1994, strong evidence of anthropogenic influence on the regional background atmosphere.

Submitted to: The Journal of Geophysical Research
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SEASONAL VARIATIONS OF SURFACE OZONE AND CARBON MONOXIDE
MEASURED AT A SUBURBAN AREA IN HONG KONG

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ABSTRACT (preliminary)

One year (1994) of O₃ and CO measurements in Hok Tusi, Hong Kong are presented. The seasonal variation of O₃ recorded is different from other measurements. The general spring peaks and winter minimum was not observed in Hok Tsui. The ozone maximum occurred in October and November (48 ppbv), which is probably caused by weak slow moving high pressure systems which underlie favorable photochemical production conditions and at the small time allow accumulation of O₃ precursors. The year-round minimum of O₃ occurred in June and July (17 ppbv). This is believed to be caused by transport of tropical marine air masses. During spring season, the ozone mixing ratio decreased from winter values gradually to the summer minimum, reflecting the gradual shift from continental outflow to maritime inflow. The absence of spring maximum suggests a secondary importance of stratospheric enhancement in the low latitudes. CO showed a similar seasonal trend with a minimum in the summer. Frequency distributions of ozone and CO are bimodal. Tropical air mass and continental air mass each possess their own characteristics which contribute to the observed bimodal feature. In the summer season, O₃ and CO are positively correlated and negatively correlated in the winter.

Submitted to the *Atmospheric Environment*

Aerosols Composition from a Rural Monitoring Site in Hong Kong --
-- Initial Results.

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ABSTRACT

The first aerosol particles samples have been collected from a rural monitoring site at Cape D'Aguilar, (22°13'N, 114°15'E, 60 meters above sea level), Hong Kong, situated on the coast of the South China Sea and the West Pacific Ocean. Inorganic compounds including sea salts and anthropogenic emissions (sulfate, nitrate and various trace elements) were measured by NAA (neutron activation analysis), XRF (x-ray fluorescence spectrometry) and IC (ionic chromatography) on TSP (total suspended particles) and RSP (PM10, respirable suspended particles). The results of the sampling program carried out in 1993 and 1994 are presented. The data obtained showed that sea salts, crustal compounds and sulfur form the highest concentration which indicate either TSP or RSP mainly consists of three parts: anthropogenic sources, sea salts and soil origins. The enrichment factor of elements of RSP are generally higher than those of TSP indicating that RSP aerosol may be related with the health of humans. The origins of particles are further discussed following enrichment factor analysis.

**WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH**

(A system for environmental pollution monitoring and research)



No. 107

**Extended Abstracts of Papers Presented
at the**

**WMO-IGAC CONFERENCE ON THE
MEASUREMENT AND ASSESSMENT OF
ATMOSPHERIC COMPOSITION CHANGE**

(Beijing, China, 9-14 October 1995)



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Trace Gas Measurements During Periods of Continental Outflow: Results From a Hong Kong Site During the PEM-WEST (B)

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Introduction

With accelerated growth in economy and human population in the Asian Pacific rim region, emissions of anthropogenic pollutants such as NO_x , SO_2 , hydrocarbons and other air pollutants have increased dramatically. For example, areas in the Pacific rim including Japan, Korea, coastal areas of China, Taiwan and Hong Kong, now rank the same as Europe and the Eastern North America in SO_2 and NO_x emissions [Atmoto and Narita, 1993]. Furthermore, it is anticipated that, in the 21st century, this region will become the largest source area of SO_2 and NO_x in the world [e.g., Galloway, 1989]. Such high and rapidly growing emissions of NO_x , SO_2 and other anthropogenic pollutants will have an adverse impact on regional air quality and may also have significant impact on the chemistry of the atmosphere over the remote Pacific. In response to these concerns and especially to the need for long-term monitoring of trace gases in the subtropical regions in Asia, a background air monitoring station was established in Hong Kong. During the study period of PEM-West Phase B (February and March 1994), intensive measurement phase was implemented during which O_3 , CO , SO_2 , NO , NO_y , total and respirable suspended particulate were measured. This paper focus on the levels and variability of trace gases, their relation to meteorological parameters, and correlation among themselves. Results on aerosol composition will be presented by Lam *et al.*

Experimental

Study Site (see figure 1)

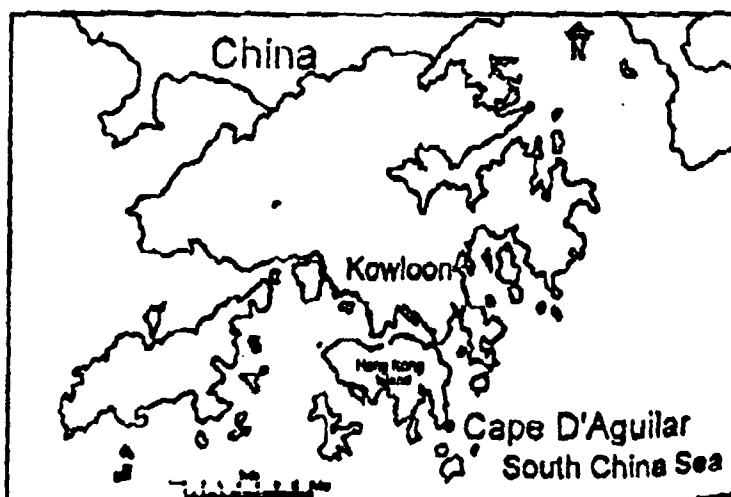


Fig. 1 Location of the site in relation to Hong Kong and China

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The measurements were made at southeastern tip of Hong Kong Island (Cape D'Aguilar, 22°13'N, 114°23'E, 60 meters MSL). The site is located in a relatively remote setting, although Hong Kong itself is highly-populated and modernized. Urban centers in the Territory are located at least 8 km northwest to the study site. In the vicinity of the site, however, there are relatively few anthropogenic activities. Instruments were housed in a modified ship container located on a cliff of 60 meters above sea level. Facing south and east of the station, is the South China Sea and the Pacific Ocean. During the study period, prevailing winds were from north and northeast, bringing in polluted air from the Chinese Mainland. Occasionally urban plumes affected the levels of trace gases at the station. Sampling inlets were mounted on a tower by the container and were approximately 4 meters above the cliff.

Instrumental methods

Ozone was measured with a commercial UV photometric analyzer (Teco 49). It has a detection limit of 2 ppbv and a precision of ± 2 ppbv.

CO was detected with an Infrared Gas Filter Correlation Analyzer (Teco 48S) with selected photomultiplier tube (PMT) for extra sensitivity. The analyzer was modified by adding a catalytic converter (0.5% Pd on alumina) for instrument background determination [Parrish *et al.*, 1991]. This modification has been proven necessary for low-level CO measurements since the analyzer is sensitive to water vapor. The detection limit was estimated to be ~ 18 ppbv for 2 minute integration time and the precision (95% confidence) was approximately 20 ppbv for ambient levels of ~ 600 ppbv.

SO₂ was measured by using a Pulsed UV Fluorescence Analyzer (Teco 43S) with selected PMT. A KOH-impregnated filter was added to determine the instrument background [Parrish *et al.*, 1991]. According to the manufacturer, detection limit for this analyzer is 0.06 ppbv for 2 minute integration and the precision is 0.10 ppbv.

NO was determined using a commercial chemiluminescence analyzer (Teco 42S). For NO_y determination, the original Molybdenum converter was relocated to the inlet system. In order to minimize the loss of "sticky" HNO₃ (a major component of NO_y), the inlet (stainless steel) prior to the catalytic converter was heated to 100 °C. The detection limit, as specified by the manufacturer, is 0.05 ppbv for 2 minute average.

Instruments were calibrated regularly by adding a small flow of standard gas to the ambient air stream at the sampling inlet (standard addition).

Results and Discussion

The data presented in the present paper cover the periods from February 17 to March 13, 1994. During this period, the meteorology of the east Pacific region was dominated by an intense low-altitude anticyclone over northern China and Siberia and a low pressure system over the Aleutian Islands, resulting in a northerly or northeasterly low-altitude flow over the east Asian coastal regions. Indeed, winds observed were predominantly from north-northeast. Temperature, dew point and trace gases showed interesting relationships with wind direction. For example, cold and dry air masses were associated with flows from north-northeast (outflow from the continent) and pollutants levels were high; on the other hand, when winds deviated

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from the prevailing directions, air arriving the site was relatively warm and humid with low levels of CO.

Day-to-day variations of ozone, CO, NO_y and SO₂ are shown in figure 2, in conjunction with time series of temperature, dew point, wind speed and wind direction. In general, levels of ozone, CO, NO_y and, to a lesser extent, SO₂ were highly variable. For SO₂ and NO_y, it appears that their variability was on a relatively short-time scale, whereas CO showed both short- and long- time variations. Continental air periodically extended its coverage to Hong Kong, and change of air mass types can be seen clearly in the following three consecutive periods: (1) 2/19-23, (2) 2/24 - 3/8 and (3) 3/9-13. Start of each period was characterized by simultaneous drops in temperature and dew coincided with enhancement in CO; air became warm and humid, and CO concentrations were reduced toward the end of the period during which the site received relatively aged continental air masses as suggested by calculated backward air trajectories on isentropic surfaces.

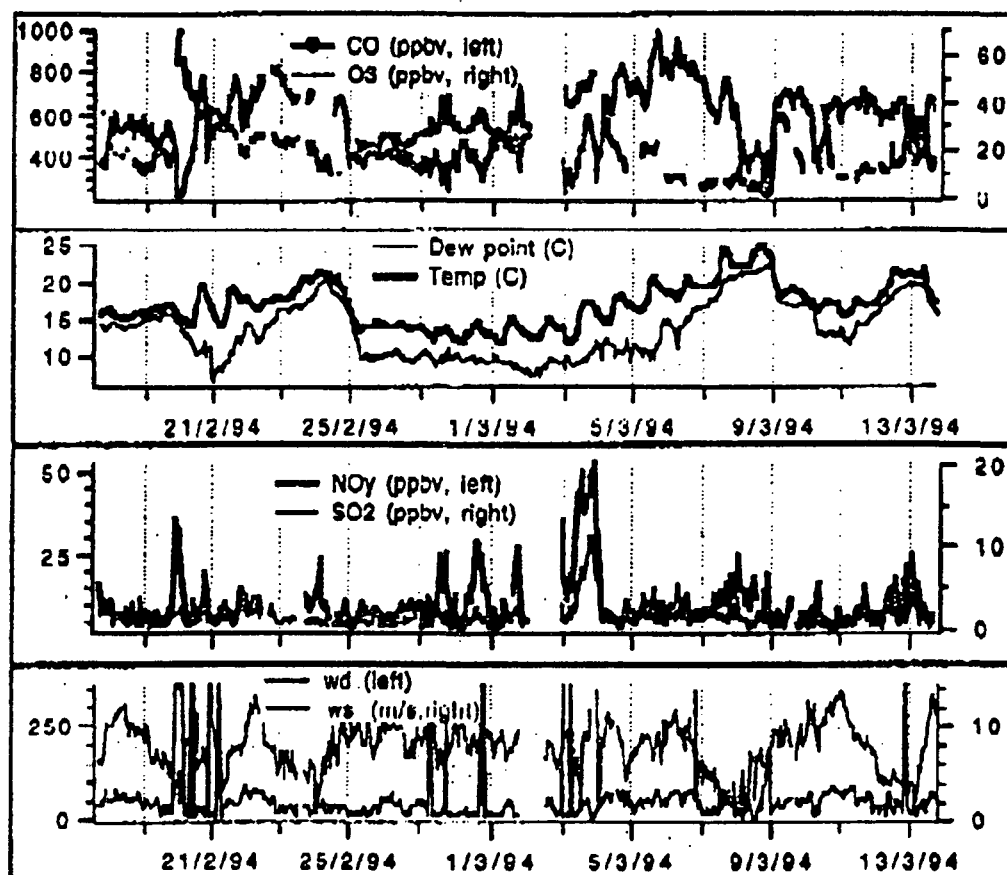


Figure 2. Time series plots

Table 1 summarizes the results of trace gases. It is noted that the levels of CO, NO_y and SO₂ here are much higher than those observed from previous studies. For example, Talbot *et al.* [1994] reported median concentrations in air parcels that left sources region (Latitude: > 20°N) for less than 2 days were 129, 0.80 and 0.22 ppbv, for CO, NO_y and SO₂, respectively. Not only the medians observed at our site are much higher than theirs, but our lowest values are higher than their maximum values.

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(expect for SO_2). The large difference may be attributed to the more intense outflow of polluted continental air mass in the winter season. Additionally, it appears that the levels of these three species are higher than those simulated for September-October periods [Shaw *et al.*, 1993].

Table 1. Summary of Trace Gas Concentrations¹

Species	Mean ($\pm$ Std ²)	Median	Range
O_3	34 (± 14)	32	1 - 67
CO	458 (± 130)	455	221 - 987
NO	1.44 (± 2.16)	1.10	0.45 - 19.8
NO_y	9.85 (± 7.83)	7.52	2.50 - 52.0
SO_2	1.31 (± 1.46)	0.95	0.031 - 11.0

¹ All concentrations are in units of ppbv.

² Standard deviation

Relationships of CO with NO_y and SO_2 were examined. Elevated CO levels were often not accompanied by enhancements of NO_y (for $\text{NO}_y < 20$ ppbv) and SO_2 , which suggests that CO and the other two species may have sometimes come from different sources and/or that long range transport may play different roles in distributing these compounds over large areas due to their different lifetimes. Here it is argued that the variability of CO (and ozone as well) was influenced by both local sources and transport of the continental sources over a long distance, whereas the variability of SO_2 and NO_y was primarily dominated by the local sources.

Relationships of ozone with CO and NO_y were examined to elucidate winter and spring-time ozone chemistry. In general, ozone was negatively correlated with CO and NO_y . The negative O_3 -CO correlation and observed high levels of CO indicate that, during initial periods of outflow, ozone was titrated by anthropogenically emitted NO (here CO is a such tracer). O_3 - NO_y relation is not as obvious as O_3 -CO, and data are more scattered for NO_y levels below 10 ppbv. This is expected if one assumes that some of the NO_y were removed from air parcels during transport. Nevertheless a overall negative O_3 - NO_y correlation existed.

Conclusions

Trace gas species including ozone, CO, NO, NO_y and SO_2 were measured at a background site in Hong Kong during periods of February 17 to March 13, 1994. Averaged concentrations determined in this study were 31 ± 14 ppbv for O_3 , 458 ± 130 ppbv for CO, 9.85 ± 7.83 ppbv for NO_y , and 1.31 ± 1.46 ppbv for SO_2 . variability in (O_3) and, to a lesser extent, ozone may be attributed to both short-range transport of urban plumes and to the long-range transport of pollutants from the continent, whereas variability in SO_2 and NO_y appeared to dominated by the processes occurred on a relatively short-time scale. CO appears to be the best chemical indicator, among the gaseous species measured, of relative intensity of the outflow from the continent.

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Ozone negatively correlated with CO and NO_y, suggesting that ozone was chemically titrated by anthropogenically-emitted NO during early stage of the continent outflow. Overall, SO₂ and NO_y correlated reasonably well and their correlation with CO is not as good. This may indicate that elevated SO₂ and NO_y may have been due to sources of common origin.

Acknowledgment

The authors would like to thank Dr. W. L. Chang of the Hong Kong Royal Observatory for providing the meteorological data, J. Merrill for providing back trajectory results for the Hong Kong site. T. Wang would like to express his gratitude to Dr. M. A. Carroll for her role in the University of Michigan's group, Dr. N. D. Sze for coordinating the collaboration between the NASA and HKPU, and to S. C. Liu for his help in the project. Technical support from the HKPU was essential to the success of the project. This research was supported by Hong Kong Polytechnic University and the U.S. NASA (through the University of Michigan).

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HKPU/NASA PEM-WEST WORKSHOP
October 18-20, 1995

TITLE: HKPU BACKGROUND AIR MONITORING - RESULTS

-Tao Wang

This presentation will focus on the initial results of trace gas measurements obtained at the Hong Kong Polytechnic University Regional Background Air Monitoring Station. Ozone, CO, NO, SO₂ have been measured since its operation in 1993. During NASA PEM-WEST B study period, preliminary NO_y measurement was conducted.

Seasonal variations of ozone and CO

One year records of ozone and CO were analyzed, and major results are as follows:

(1) CO concentrations show a maxima in the winter and a minima in the summer, spring- and fall values being in the transition. This is consistent with the general meteorology in the east Asia region- outflow of continental air is predominant in the winter, and prevailing winds in the summer are from above the oceans. Ozone median concentrations exhibited a summer minima and a maxima in the fall.

(2) There is diurnal trend for ozone in the spring, fall and winter: ozone median concentrations are higher than night-time values by about 15 ppb, suggesting the contribution of photochemical production of ozone. Median ozone concentrations in the summer are low (~ 20ppbv) and show little diurnal variations, suggesting much less degree of ozone production in the averaged air masses encountered. O₃-CO relationship is driven by the two processes-photochemical production of ozone by anthropogenic precursors yields a positive correlation whereas ozone titration by anthropogenic pollutants (NO_x and VOCs) gives a negative correlation.

Results from the Intensive during the PEM-WEST study period.

Ozone, CO, NO, NO_y and SO₂ data were analyzed for the study period of the PEM-WEST B Experiment (February-March 1994). Concentrations of these species were strongly influenced by the continental outflow from Asia and particularly by the passages of cold fronts which periodically brought high levels of pollutants from the North. Averaged concentrations are 31 ± 14 ppbv for O₃, 458 ± 130 ppbv for CO, 9.33 ± 7.84 ppbv for NO_y, and 1.31 ± 1.46 ppbv for SO₂. CO appeared to be a good chemical indicator of changes of air mass types and its variability may be attributed to the relative strength of the outflow and to the transport of urban plumes. Variations of NO_y, SO₂ and black carbon appeared to be dominated by processes that occurred on relatively short time scales. Ozone was negatively correlated with CO and NO_y, suggesting that O₃ is chemically titrated by anthropogenic pollutants during the early stage of continental outflow.

Photochemical Ozone Episodes

Although the Station is not normally downwind of the Hong Kong urban centers (prevailing winds are from the East and Northeast), it captured four ozone episodes in 1994, during which hourly-ozone mixing ratios reached > 80 ppbv (in one case ozone reached as high as 170 ppbv). During these episodes, surface winds switched to northerly, and anthropogenic pollutants such as CO, SO₂ and reactive nitrogen were also elevated. It is expected that in other locations that are more often downwind of urban areas, such photochemical ozone episodes may be more pronounced.

Some on-going and future study topics include:

- (1) Summer-time atmospheric chemistry of ozone and its precursors. The air masses encountered in the summer sometimes represent those characteristic of regional background conditions.
- (2) Long range transport of air pollutants to Hong Kong, especially during spring and fall when the Station is upwind of the Hong Kong urban areas.
- (3) Meteorological conditions during the ozone episodes, and the relationships with urban ozone concentrations.